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PROCESSING AND THERMAL CONDUCTIVITY OF CARBON NANOTUBE-REINFORCED NICKEL MATRIX COMPOSITES (PREPRINT)

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14. ABSTRACT
Multi-wall carbon nanotube (MWCNT)-reinforced nickel composites have been manufactured in a bulk form by using a laser deposition technique, commercially known as the laser engineered net shaping (LENS™) process. These nanocomposites have been characterized in detail by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and high-resolution TEM study has also been conducted on these nanocomposites to characterize the nanotube/metal matrix interface. In addition, the thermal conductivities of Ni/CNT composites deposited by the LENS™ process have been measured by using Fourier Law of conduction in vacuum. The measurement did not show enhancement of thermal properties, which is caused by the inherent formation of voids and carbide formed during the LENS™ process.

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PROCESSING AND THERMAL CONDUCTIVITY OF CARBON NANOTUBE-REINFORCED NICKEL MATRIX COMPOSITES

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ABSTRACT

Multi-wall carbon nanotube (MWCNT)-reinforced nickel composites have been manufactured in a bulk form by using a laser deposition technique, commercially known as the laser engineered net shaping (LENS™) process. These nanocomposites have been characterized in detail by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and high-resolution TEM study has also been conducted on these nanocomposites to characterize the nanotube/metal matrix interface. In addition, the thermal conductivities of Ni/CNT composites deposited by the LENS™ process have been measured by using Fourier Law of conduction in vacuum. The measurement did not show enhancement of thermal properties, which is caused by the inherent formation of voids and carbide formed during the LENS™ process.

1. Introduction

Carbon nanotubes (CNTs) as reinforcements in metal matrices offer attractive properties such as mechanical, electrical and thermal properties of these novel composite materials [1-3]. Single walled or multi walled CNTs are being used for reinforcing a number of materials systems including polymeric, metallic and ceramic matrices. There are huge researches regarding polymer based composites, while relatively fewer studies have been devoted to metal based composites. Recently, new processing technique using laser engineered net shaping (LENS™) process has been employed to fabricate metal matrix-based composites and also addressed the issues regarding distribution, stability and interfacial bonding of the nanotubes in the metal matrix [4]. The advantage of processing such metal-matrix nanocomposites using LENS™ is two-fold. Firstly, it is possible to obtain bulk CNT-metal nanocomposites without significant damage to the CNTs, thus abating the limitation of large-scale production inherent in other techniques such as molecular level mixing. Secondly, being a liquid-based processing route, LENS™ deposition does not suffer from some of the disadvantages inherent in conventional powder processing techniques, such as enhanced porosity. Hwang et. al. has compared Ni-CNT nanocomposites with Ni-graphite composites, both being processed by using LENS™ technique [5]. This study clearly indicates the substantially higher stability of CNTs as compared with graphite, during processing in a molten nickel matrix. The LENS™ process using the pre-mixed powder via ball-milling process has been employed to fabricate CNT/Ni composites, including attempts to identify the strengthening mechanism involved. The bimodal distribution of CNT in the nickel matrix as an individual and bundle-like CNTs dispersion in the Ni matrix composites have showed great improvement of the mechanical properties [6]. Thus, the laser deposition technique is considered as a promising manufacturing technique for CNT reinforced metal matrix composites. While many researchers studied on the mechanical properties, very few researches are performed on thermal conductivity on the metal/CNT composites [7-8]. Therefore, this study has been focused on the following important issues:

1. Manufacturing the Ni/CNT composite with laser engineered net shaping techniques with well distributed carbon nanotube in the nickel matrix.
2. Established the experimental setup for measuring the thermal conductivity of metal/CNT composites.
3. Characterization of the microstructure and thermal properties on the Ni/CNT composites.

2. Experimental Procedure

2.1. Sample preparation of LENS deposition

The Multi-walled CNTs processed by chemical vapor deposition techniques with a purity of ~90% were used for reinforcing materials. From the TEM analysis on the raw MWCNT, the length of MWCNTs was found to be ~10 microns. The Ni powder used in the study was procured from Crucible research and was in the form of spherical particles with diameter ranging from 44-149 microns. The detailed information of the raw materials used in this experiment was reported elsewhere [5].

The steel substrate was used for deposition of composites. The LENS™ process uses a powder feedstock as an input material. The process begins with a CAD design file, which is post-

processed into a series of 2D layers. To provide the best build, each successive layer was deposited in a scan direction that was different from the previous layer to ensure homogeneity. A high-energy pulsed Nd:YAG laser, emitting near-infrared laser radiation at a wavelength of 1.064 μm, is focused on the substrate to create a melt pool into which the powder feedstock is delivered through an inert gas flowing through a multi-nozzle assembly. The powders used in this study consisted of CP-Nickel and 5 wt.% MWCNT. A smooth flow of metal powder is required to form a good deposit. Therefore, instead of mixing CNT and Ni *in situ*, these powders were premixed (Ni+5wt.% MWCNT) by ball milling for 48 hours using two different sizes of tungsten carbide balls of diameter 0.5 and 0.25 inches to obtain a homogenous mixture of the pre-mixed powder, which subsequently was fed into the powder feeder of the LENS system. A 300W laser power having 30A high-current pulsed laser was used to deposit the bulk composite. The schematic diagram of the LENS process is shown in Fig. 1. The Ni/CNT composite was deposited into cylindrical shape with 0.5 inch diameter and 1 inch length. The LENS deposited sample was milled into 9.5 mm diameter and 20 mm length to get even surface for thermal conductivity sample. Four blind holes were drilled along the length of cylinder to insert thermocouple to measure the temperature gradient.

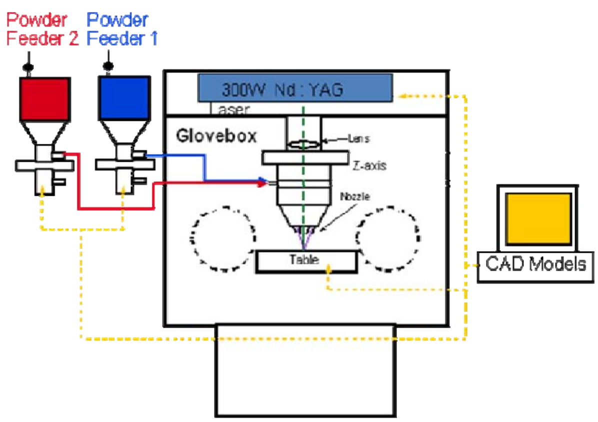

Fig. 1. Schematic diagram of the laser engineering net shaping (LENS™) system.

To observe the microstructure analysis the deposited samples were cut and sectioned using the diamond cutter. These samples were mounted and mechanically polished for metallographic studies. All the SEM studies of the as-deposited nickel-CNT composite were done on FEI Quanta ESEM. A standard TEM sample was made and characterized using FEI/Philips E-420 microscope and FEI TECHNAI F20 field emission gun microscope operating at 120 and 200 kV respectively.

2.2 Setup for thermal conductivity measurement

The measurement of thermal conductivity is based on one-dimensional Fourier law of conduction:

$$Q = -kA\frac{dT}{dx} \quad (1)$$

One dimensional assumption is valid because the silicon substrate (with high thermal conductivity of 130 W/mK) maintains at uniform temperature by generating joule heating essentially on the entire substrate of the thin-film microheater as shown in Fig. 2. To make sure the heat flow is only through the cylindrical sample, we performed the experiment in vacuum where we can neglect the conduction loss from the sample. Furthermore, the surface temperature of the heater is maintained below 40 ^{o}C in which the radiation heat transfer loss from its surface can be neglected. The heater temperature was obtained by applying known current through the heater and measuring the voltage as shown in Fig. 2. A temperature-resistance calibration curve was obtained in a uniform-temperature thermal reservoir (not shown in Fig. 2) to obtain the temperature of the heater. The current source and voltmeter used in this experiment are Keithley 6221 and Keithley 2180, respectively.

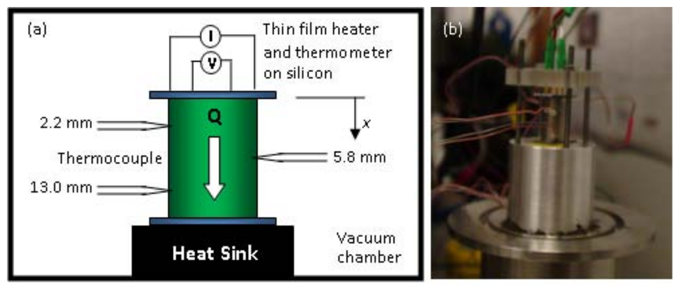

Fig. 2 (a) Schematic diagram of experimental setup and (b) photograph of actual setup

A simple analysis turns out that estimated maximum radiation heat loss from the heater is within 3% by assuming emissivity of 0.7 (maximum average value) at room temperature and using Stefan-Boltzmann law,

$$E = \varepsilon\sigma\left(T^4 - T_{sur}^{\ 4}\right) \quad (2)$$

Essentially there is no radiation heat loss from the sample (Ni-CNT composite) because of very low emissivity of Ni (0.05, majority component of the composites). Therefore, the heat flow can be calculated by $Q=I^2R$ where I is the applied current and R is the resistance of the heater. To measure the temperature gradient through the sample, we embedded three thermocouples (E type) along the cylinder (see Fig. 2). The standard deviation of the temperature measurement ranges 0.2-0.4 ^{o}C (depending on the position). The physical dimension of the sample is given in Fig. 2. This dimension is used in the discussion to calculate the thermal conductivity. All the data analysis including mean and standard deviation of the temperature were obtained through LabVIEW interface.

3. Results and Discussion

3.1 Microstructure of Ni/CNT composite

Prior to laser deposition, the ball milled mixture of Ni/MWCNT powders observed by scanning electron microscopy (SEM) was shown in Fig. 3. As shown in Fig. 3 It is evident from the secondary electron image, shown in Figs. 1(a), individual and cluster types of CNTs are observed after mechanical milling, which helps mechanical adhesion of these nanotubes on the surface of the spherical Ni powder particles.

From the higher magnification SEM study on the Ni-CNT powder revealed separated bundles of nanotubes in the size range of 3 – 20 μm as well as individual nanotubes or clusters sticking on the surface of the Ni powder particles.

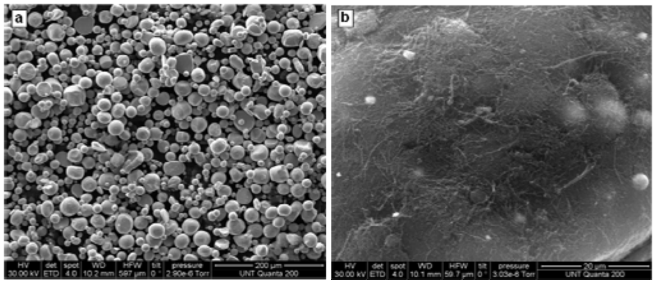

Fig. 3. (a) Ni powder before the ball milling, and (b) individual and cluster nanotube attached on the Ni particles after ball milling.

The back scatter SEM microstructure of the composite after LENS™ has shown in Fig 4(a). This image shows a homogeneous distribution of near-spherical carbon-rich regions (darker contrast) uniformly distributed in the nickel matrix (brighter contrast). The energy dispersive spectroscopy (EDS) results reveal that the composition of these regions presents only carbon in the darker spherical regions. The LENS™ deposited composite did not exhibit larger bundles more than 20 μm range, which suggest that further breakdown of the nanotube agglomerates occurs during laser deposition process. It is believed that ball milling process with high shear stresses during the powder mixing break up into smaller bundles that physically adhere to the surface of nickel powder particles. This pre-mixed balling process combined with the instantaneous melting and deposition of the nickel powders results in well distribution of nanotube bundles within the nickel matrix. The homogeneous and refined carbon-rich regions inside the nickel matrix are clear evidence of the advantage of ball milling, overcoming the limitations associated with the density difference between nickel and carbon nanotube powders. The high temperature stability of carbon nanotubes in the molten nickel metal permits them to retain their chemical identity even after being melt processed. However it is difficult to confirm the structural identity of these carbon-rich regions based purely on the SEM analysis and therefore further detailed examination at higher magnification is required in order to fully understand the structure, morphology and chemistry of these bundles.

In order to observe the higher magnification on the structure of these carbon rich regions, transmission electron microscopy (TEM) sample of this region was prepared. Fig. 4(b) shows the bright field TEM images of the Ni/CNT bundle area, which is corresponding to the dark region in Fig. 4(a). The higher magnification TEM image of bundle shows that CNTs are overlapped and intertwined with each other. The Fig. 4(b) shows that clear evidence of CNT bundle shows sharp interface. The figure shows that CNTs have good contact with nickel matrix suggesting good bonding between two different materials. It is believed that bundle type of CNTs or individual CNTs in the nickel matrix enhance the mechanical properties as well as thermal conductivity.

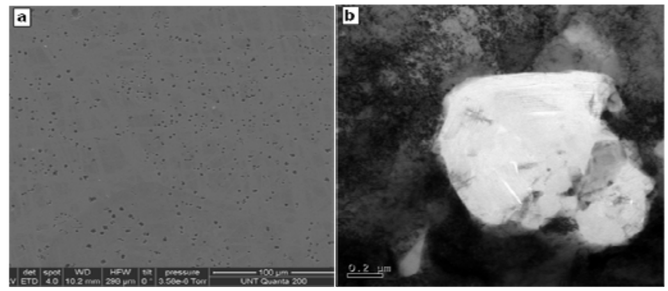

Fig. 4. Back-scatter SEM image of Ni/CNT composite showing uniform distribution of carbon rich region (dark color), and (b) bright field TEM image of carbon rich region corresponding to dark color region in figure (a).

3.2 Thermal conductivity property

Fig. 5 shows measured temperatures at each position indicated in Fig. 2. Using Eq. 1, thermal conductivity of the sample can be obtained. The measured average temperature shows a good linear behavior, which validates the one dimensional Fourier Law. The measured thermal conductivity of the composite turns out to be 3 times smaller than the bulk nickel at room temperature (see Table 1). The main reason for an opposite trend to what is expected is due to the fabrication method in which voids remain in the sample, leading to tortuous path to thermal energy flow. Yamanaka et al. reported that thermal conductivity was found to increase by 10 % with 3vol% MWNT/Ni composite [7]. However, the formation of carbide and oxide is believed to diminish the thermal conductivity in this study. Therefore, the detail analysis on the microstructure and improving measurement need to be carefully explored.

Table 1. Thermal conductivity measured using experimental setups from Fig. 2.

Current (mA)	Resistance (Ω)	Diameter (mm)	$\Delta T/\Delta L$ (^{o}C/m)	Thermal conductivity (W/m^{o}C)
30.0	314±1	9.5±0.08	-142.9	27.8
35.0	317±1		-183.5	29.9

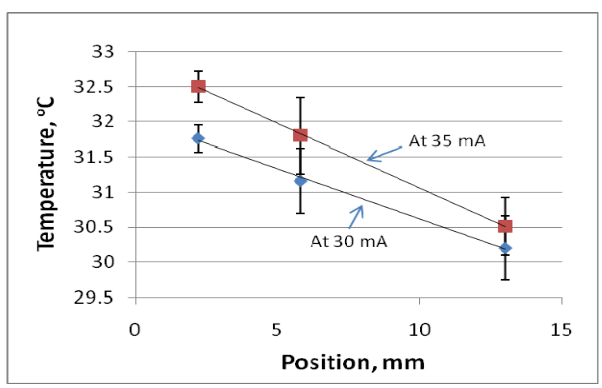

Fig. 5. Measured temperature as a function of distance from the film heater and thermometer.

4. Conclusions

Nanocomposites based on a nickel matrix reinforced with carbon nanotubes have been deposited using the laser engineering net shaping techniques (LNES). A pre-mixed powder consisting of nickel particles and MWCNTs was prepared prior to laser deposition by the ball milling process, resulting in a more homogeneous distribution of the nanotubes in the nickel matrix. From the microstructure CNTs are homogenously distributed and have sharp interface in the nickel matrix showing good adhesion. The thermal conductivities of Ni/CNT composite decreased due to the formation of voids and carbides.

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